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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

### Mechanistic Investigation of osmium(VIII) catalyzed oxidation of glutamic acid with sodium salt of N-chloro 4-methylbenzenesulfonamide in aqueous media A Practical Approach

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Accepted author version posted online: 14 Jan 2015.

To cite this article: Aftab Aslam Parwaz Khan, Anish Khan, Abdullah M. Asiri, Naved Azum, Malik Abdul Rub, Mohammed M. Rahman & Sher Bhadar Khan (2015): Mechanistic Investigation of osmium(VIII) catalyzed oxidation of glutamic acid with sodium salt of N-chloro 4-methylbenzenesulfonamide in aqueous media A Practical Approach, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, DOI: <u>10.1080/15533174.2013.872141</u>

To link to this article: <u>http://dx.doi.org/10.1080/15533174.2013.872141</u>

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# Mechanistic Investigation of osmium(VIII) catalyzed oxidation of glutamic acid with sodium salt of N-chloro 4-methylbenzenesulfonamide in aqueous media: A Practical Approach

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**Keywords** Osmium(VIII), Glutamic acid, N-chloro 4-methylbenzenesulfonamide, Kinetics and mechanistic dicussed

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### ABSTARCT

L-glutamic acid, used in the production of monosodium glutamate spices and other biochemical reagents. Its oxidation kinetics and a detailed mechanistic interaction of Os(VIII) catalyzed Glue-CAT reaction in alkaline medium have been investigated at different tempretures. It has been studied spectrophotometrically as a basic experimental approach for this study. All variables affecting the development of the color were investigated and the conditions were optimized. The effect of Glue, CAT, Os(VIII) and OH concentration on the rate of reaction has been studied. The reactions follow identical kinetics for all It is a first order reaction in both Glue and CAT, but fractional order in alkali and Os(VIII). Increasing ionic strength dielectric constant of the medium had no significant effect on the rate. The effects of added products like halide ions and Toluene-p-sulphonamide have also been investigated. A mechanism involving the formation of a complex between Glue-CAT-Os(VIII) has been proposed. The stoichiometry of the reaction is found to be 1:1. The main products of Glue were identified with the help of FTIR and TLC. The reaction constants involved in the mechanism are explained. There is a good agreement between the observed and calculated rate constants under different experimental conditions. Investigations at different temperatures allowed the determination of the activation parameters with respect to the slow step of the proposed mechanism. The proposed methods were successfully applied for the high yield of the products and short reaction times. It is also an inexpensive simple and smooth method.

### INTRODUCTION

Oxidation of amino acids is of immense significance both from chemical view point and from its behavior on the mechanism of amino acid metabolism. Amino acids not only act as building blocks in protein synthesis but also play a significant role in the metabolism. They are subjected to many reactions and can supply precursors for many endogenous substances like hemoglobin in blood. They can undergo many kinds of reactions, depending on whether a particular amino acid contains a polar or non-polar subtituent. L-Glutamic acid is one of the most abundant amino acids, especially high in cereal proteins and can be oxidized by different oxidants [1-6]. A salt of glu-e is used in the production of monosodium glutamate and nutritional supplements. L-glutamate itself can be used as medicine and promotes oxidation process. It combines with ammonia as a drug-free glutamine. It is mainly used for the treatment of hepatic coma and severe liver dysfunction, but the response is not satisfactory. Racemic glutamate is used for the production of drugs. Physiologically, it plays a role in the metabolism of amino groups and is the precursor of neurotransmitter, gamma-amino butyric acid and L-glutamic acid. Being acidic in nature it is important in determining 3-D conformation of proteins.

The well-known member of this group, chloramine-T(*p*-Me-C6H4SO2NClNa.3H2O or CAT), is a well known analytical reagent, and the mechanistic aspects in many reactions have been reported [7-11]. The redox potential of CAT is pH dependent and decreases with an increase the medium of the pH [12]. The nature of active oxidizing species of CAT depends on the pH of the medium and the reaction circumstances. Chloramine-T is a source of positive halogen and this reagent has been exploited as oxidant for a variety of substrates in both acidic

and alkaline media [13-18]. We have also observed that the oxidation of LF by CAT in alkaline medium [19].

The OsO4 undergoes reduction up to +2, +4 and +6 oxidation states in acid medium. However, in alkaline medium it undergoes reduction [20] up to +6 oxidation state only. Together the unique nature and the moderate reduction potential, [21] Os(VIII)/(VI) of +0.85 V in acidic and +0.30 V in aqueous medium act as a catalyst with a large number of oxidants both organic and inorganic substrates[22]. Hence, this study is concerned with the mechanistic to setup the oxidative paths of L-glutamic acid. with a N-chlorobenzenesulfonamide oxidant and a catalyst, osmium(VIII), respectively.

### EXPERIMENTAL

### **Chemicals and Solutions**

Stock solution of L-Glutamic acid (Merck) was prepared by dissolving known amount of its hydrochloride salt in distilled water. Chloramine-T ( E. Merck ) was purified by the method of Morris et al. [23]. An aqueous solution of CAT was prepared, standardized periodically by the iodometric titration, and stored in brown bottles to prevent its photochemical deterioration. All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts in doubly distilled water. A stock solution of Os(VIII) (BDH) was prepared in 0.50 mol dm–3 NaOH and its concentration was standardizing by titrimetric method against ceric sulphate solution [24]. Acetonitrile (Sigma) and acrylonitrile (Sigma) were used directly as received to study for the effect of solvent polarity in varying proportions (v/v) of water-

acetonitrile mixtures on the reaction medium and free radical formation, respectively. NaOH and NaClO<sub>4</sub> were used to provide the required basicity and to maintain the ionic strength respectively.

### **Instruments Used**

The absorption spectra were obtained with UVD-2960 Double beam PC connected UV–vis spectrophotometer. All potentiometric measurements were carried out with EL20 Education Line pH Meter from Mettler-Toledo Inc. IR spectra of the products was scanned with Spectrum 100 FTIR spectrometer (PerkinElmer).

### **Kinetic Studies**

All the kinetics measurements were studied under pseudo first-order conditions at a room temperature. The reaction was initiated by mixing the previously thermostated solutions of Glu-e and CAT, which also contained the required amount of NaOH, sodium perchlorate, osmium(VIII) and doubly distilled water. The temperature was maintained at 25 °C. All measurements were completed in glass Stoppard Pyrex boiling tubes coated black to do away with photochemical property. The progress of the reaction was monitored estimating the amount of unconsumed CAT by measuring the spectrophotometric method recorded by a UVD-2960 Double beam PC connected UV–vis spectrophotometer. The pH of the reaction mixture was found to be always the same pH at the beginning and end of the runs. The pseudo-first order rate constants, k<sub>obs</sub> obtained from the slope of the plots of log(absorbance) versus time were linear (Fig.3). The kinetic runs were followed for more than 80% completion of the reaction and good first order kinetics were observed. Regression analysis of the experimental data to obtain the regression co-efficient, r was performed using origin Software.

### **Stoichiometry Reaction and Product Analysis**

The reaction mixtures containing an excess of CAT over Glue in the presence of NaOH and Os(VIII) catalyst were kept were kept at 25°C for 72 h. The amount of the residual CAT in reaction mixture was determined spectrophotometrically. The reaction may be represented by the following scheme 1.

From the scheme 1 showed that the ratio of one mole Glue consumed per mole of CAT in the presence of catalysts was found to be 1:1 and the product CAT-Glue-Os mixture in the form of stoichiometric ratio under stirred condition was satisfactory to run for 72 h at 25°C. After completion of the stirring the reaction products checked by TLC, and extracted with ethyl acetate . The main reaction products 4-oxobutanoic acid and *p*-toluenesulfonamide (TsNH2), were identified and characterized by FT-IR. The v(C=O) appears at 1612 cm<sup>-1</sup> which is the characteristic band of aldehyde and also *p*-toluenesulfonamide was detected by TLC (Rf=0.910).It does not undergo further oxidation. Ammonia was identified by Nessler's reagent. The CO<sub>2</sub> liberated was detected by passing the gas into lime water.

### **RESULTS AND DISCUSSION**

### Effect of Varying oxidant Concentrations on the rate

With invariable concentration of [Glue],  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>, and [OH<sup>-</sup>]  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>, at constant ionic strength, 0.10 mol dm<sup>-3</sup>, the CAT concentration was varied in the range of  $1.0 \times 10^{-4}$  – $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>. All kinetic runs exhibited identical characteristics. The linearity of plots of log (absorbance) vs time, for different concentrations of CAT, indicates order in CAT concentration as unity. This was also confirmed by the constant values of pseudo first order rate constants, k<sub>obs</sub>, for variable [CAT] (Table 1).

### Effect of Varying Substrate Concentrations on the rate

The concentration of Glue was varied in the range of  $5.0 \times 10^{-5}$  to  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup> with all other conditions being constant at 25 °C. The substrate [Glue] concentration The k<sub>obs</sub> increased with increase in the concentration of [Glue] but it was found to be less than unity (Table1).

### Effect of Varying basicity Concentrations on the rate

The oxidation of [Glue] by CAT was studied at varying concentrations of OH- by keeping other conditions constant. The rate of oxidation increased with increase in the concentration of OH(Table1).

### Effect of Varying Catalyst Concentrations on the rate

All parameters keeping constant with catalyst Os(VIII) concentration was varied in the range of  $5.0 \times 10^{-6}$  to  $5.0 \times 10^{-5}$  mol dm<sup>-3</sup> draw the plots of log [Os(VIII)] versus log  $k_{obs}$  with linear slopes showed a rate increased with increases [Os(VIII)] that means fractional-order dependence on [Os(VIII)] (Table 1).

### Effect of Varying Ionic Strength and Dielectric Constant Concentrations on the rate

The effect of ionic strength was studied by varying the NaClo4 concentration from 0. 10 to 0.40 mol dm<sup>-3</sup> at constant concentrations of CAT, Glue,Os(VIII) and alkali. Increasing ionic strength had no effect on the rate constant. The effect of the dielectric constant (*D*) was studied by varying the MeOH-water content (v/v) in the reaction mixture with all other parameters constant. The rate of reaction decreases with increasing MeOH volume(Table 2). The plot of log  $k_{obs}$ 

versus 1/*D* was linear with negative slope following a rate-limiting step with partial ionization. Such type values of dielectric constant of MeOH-H2O mixture reportede[25] were employed

### **Effect of Added Product.**

The effect of initially added product, Toluene-p-sulphonamide was studied in the  $1.0 \times 10^{-4}$ – $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> concentration range, keeping the ionic strength, reactant concentrations, and other conditions constant. No significant effects on the reaction rate as observed.

### Additon of halide ions Concentrations on the rate

The effect of halides ions(NaCl and NaBr) on the rate of reaction was studied at constant other parameters concentration, the addition of did not show any effect on the rate. These results indicate that the halide ions play no role in the reaction mixture

### **Free Radical Study**

The intervention of free radicals was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for 1 h. When the reaction mixture was diluted with methanol, no precipitate resulted, indicating the absence of free radicals in the reaction mixture.

### **Effect of Temperatures**

The effect of temperature on the reaction rate was studied for all the kinetic runs at four different temperatures (20-37°C), keeping other experimental conditions constant. The activation parameters (*Ea*,  $\Delta H^{\#}$  and  $\Delta S^{\#}$ ) corresponding to these rate constants have been evaluated from the Arrhenius plot of log k versus 1/*T* from which other activation parameters were also obtained (Table 3)

### **Reactive Species of Os(VIII)**

In general, osmium is widely used as a catalysis agent where the reactions are governed by the medium of pH. Of all the oxidation states of osmium +8 is the most potent state in alkaline media [26-28]. In strongly alkaline medium, osmium behaves different types of the complexes such a OsO4,[OsO4(OH)(H2O)], [OsO4(OH)2]<sup>-</sup> and [OsO5(OH)]<sup>3-</sup> coexist in fast equilibrium.

$$OsO_4 + OH^- + H_2O = [OsO_4OH(H_2O)]^-$$
(i)  
$$[OsO_4OH(H_2O)] \stackrel{-}{+} OH^- = [OsO_4(OH)_2]^{2-} + H_2O$$
(ii)  
$$k_{obs} = k_o + k_C [catalyst]^x$$

Both the octahedral complexes racting ineffective with an oxidant. It is realistic to assume that OsO4 and the basic geometry of OsO4 molecules is tetrahedral. It is the active catalyst to form a complex with this oxidant[29-31].

### **Reactive species of CAT**

In general, CAT undergoes a two-electron change in its reactions forming the reduction products, TsNH<sub>2</sub> and sodium chloride. The oxidation potential of CAT–TsNH<sub>2</sub> varies with medium of the pH [32]. CAT behaves different types of reactive species in solution[33-34].

TsNClNa  $TsNCl^{-} + Na^{+} (i)$ TsNCl<sup>-</sup> + H<sup>+</sup> TsNHCl (ii)

(CAT) (where, Ts represents CH3C6H4SO2-group).

Thus, CAT exists as a free acid (TsNHCl) in acidic media. The dissociation constant of TsNHCl at a pH ca. 4.5 is  $2.8 \times 10^{-5}$  reported by Morris et al. [22]. Further, TsNHCl can undergo disproportionate or hydrolysis according to following reactions [35]:

2 TsNHCl 
$$\longrightarrow$$
 TsNCl<sub>2</sub> +TsNH<sub>2</sub> (iii)  
TsNHCl + H2O  $\longrightarrow$  TsNH<sub>2</sub> +HOCl (iv)  
TsNHCl + H+  $\xrightarrow{}$  TsNH<sub>2</sub>Cl<sup>+</sup> (v)  
TsNH<sub>2</sub>Cl<sup>+</sup> +H2O  $\xrightarrow{}$  TsNH<sub>2</sub> + (H<sub>2</sub>OCl)<sup>+</sup> (vi)

It appears from the equilibrium (i)–(vi), that various probable oxidizing species of CAT exists in acidic media such as TsNHCl, TsNCl<sub>2</sub>,TsNH<sub>2</sub>Cl, TsNH<sub>2</sub>, HOCl and H<sub>2</sub>OCl<sup>+</sup>.

In alkaline medium CAT exists such as TsNHCl, HOCl and TsNCl<sup>-</sup> reported by Johnston [36] according to following equation

$$T_{sNCl- + H2O} \longrightarrow T_{sNHCl + OH} (vii)$$

$$T_{sNHCl + H_{2O}} \longrightarrow T_{sNH_{2} + HOCl} (Viii)$$

In the present work, the rate dependence on  $[OH^+]$  that the TsNCl- formed from TsNHCl results for the formation of TsNHCl, which is a probable oxidizing species involved in the oxidation of Glue in alkaline medium Scheme 1.

A detailed mechanistic explanation of Glue–CAT-Os in alkaline medium is given in Scheme 2. In view of the observed experimental results, (TsNHCl) is considered to be the active species. The fractional order dependence of Pseudo first-order rate constant on OH- that means

preequilibrium step with CAT formed anion species TsNCl- from TsNHCl, which resulted for the oxidation of Glue by CAT in aqueous condition.

It was confirmed by varying Os(Viii) concentration which result inverse first-order rate constants,  $k_{obs}$ . The rate was increased with increase Os(VIII) concentration(Table 1)and the order of the reaction was determined from a log with linearty. It indicates a unit order dependence on Os(VIII) concentration.

Keeping all other conditions constant the concentrations of the oxidant TsNHCl, substrate (Glue), catalyst Os(Viii) and alkali was varied. The reaction fallowed the first-order. Based on the experimental results, a mechanism can be proposed for which all the observed orders for each constituent such as [oxidant], substrate, catalyst and [OH<sup>-</sup>] may be well accommodated. The kinetics of Os(VIII)-catalysed Oxidation of Glue by TsNHCl in in aqueous alkaline medium is a non-complementary reaction with oxidant undergoing five equivalent changes. Added acrylonitrile did not undergo polymerization under inert atmospheres that means absence of free radical in this reaction system.

Pseudo first-order rate constant dependent on the concentrations of both CAT and Glue and the fractional-order dependence on the [OH-] and inverse in [Os(VIII)] that means an intermediate complex is formed from the [Os(VIII)] and CAT and then interacts with the substrate. In light of these considerations, Os(VIII) catalyzed Glue-CAT oxidation mechanism was explained, as shown in Scheme 3.

It appears that the alkali combines with TsNHCl to give anion species TsNCl- <sup>·</sup> In the second step, TsNCl- combines with Os(VIII) to form an intermediate complex X. The variable order with respect to Os(VIII) most probably results from the complex formation between oxidant and

catalyst prior to the substrate step. Further evidence was obtained from the UV–vis spectra of reaction mixtures. Spectrophotometric results can be verified of an intermediate complex A(A hypsochromic shift, of complex A ca. 5 nm from 320 to 315 nm is observed in case of Os(VIII)- and Os(VIII)-CAT mixture ). Analogous effects upon complex formation between a catalyst and an oxidant have been observed in other investigations [37]. A obtained oxidant catalyst complex react with substrate to give another intermediate Complex C. Complex C decomposes in slow step to give the product of Glue.In a further fast step, one molecule of formed Oxidant-Catalyst reacts with one more molecule of glu-e bring the oxidation of Glue to yields final product of Glue as 4 oxo butonic acid (Scheme 2).The ratio can be satisfying the stoichiometry and such a catalyst substrate complex was obtained from the spectrophotometric measurements. The formation of this complex was proved kinetically by Michaelis–Menten plot, i.e., a non-zero intercept plots(Fig.3).A high rate constant for the the large rate constant slow step, point out the oxidation most probably occurs by the use of an inner-sphere mechanism [38,39]

A detailed mechanistic interaction of Os(VIII) catalyzed Glue-CAT reaction in alkaline medium is showed in Scheme 2, in which the structures of complex intermediate species Complex A are given.

The total effective concentration of CAT can be written from From rate detemining step (Scheme 2):

 $[CAT]_{t} = [TsNHCI]+[TsNCI] + [X]+[Complex (C)]$ (1)

which leads to the following rate law:

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$$[CAT]_{t} = \frac{-d[CAT]_{t}}{dt} = \frac{K_{1}K_{2}K_{3}[CAT]t[Glue][OH^{-}][Os(VIII)]}{1+K_{1}[OH^{-}]+K_{1}K_{2}[OH^{-}][Os(VIII)]}$$
(2)

Further rate law equation (2) is in agreement with the experimental data.

Since rate =  $k_{obs} = [CAT]t (3)$ 

Rate law equation (2) can be substituted in equation (3) and explains all the observed rate constant of different type Equation can be rearranged in the following form.

$$k_{obs} = \frac{K_1 K_2 K_3 [G | u e ] [O H^{-}] [O s (V | ||)]}{1 + K_1 [O H^{-}] + K_1 K_2 [O H^{-}] [O s (V | ||)]}$$
(4)

$$\frac{1}{K_{obs}} = \frac{1}{K_1 K_2 K_3 [Glue] [OH^{-}] [Os(VIII)]} + \frac{1}{K_2 K_3 [Glue] [Os(VIII)]} + \frac{1}{K_3 [Glue]}$$
(5)

$$\frac{1}{k_{obs}} = \frac{1}{[OH^{-}]} \left\{ \frac{1}{K_{1}K_{2}K_{3}[Glue][Os VIII]} \right\} + \left\{ \frac{1}{K_{2}K_{3}[Glue][OH^{-}]} + \frac{1}{K_{3}[Glue]} \right\} \sim 6.$$

$$\frac{1}{K_{obs}} = \frac{1}{[O_{s} VIIL]} \left\{ \frac{1}{K_1 K_2 K_3 [Glue] [OH^-]} + \frac{1}{K_2 K_3 [Glue]} \right\} + \frac{1}{K_3 [Glue]} \sim 7.$$

A plot of  $1/k_{obs}$  versus 1/[OH] from the equation ( 6) gives

Slope = 
$$\frac{1}{K_1 K_2 K_3 [\text{ Glue}] [\text{ Qs-VIIL}]}$$
 Slope =  $\frac{1}{K_1 K_2 K_3 [\text{ Glue}] [\text{ Qs-VIIL}]}$ 

Intercept = 
$$\frac{1}{K_2 K_3 [\text{ Glue}] [\text{ OH}^-]} + \frac{1}{K_3 [\text{ Glue}]}$$

Similarly, a plot of 1/kobs versus 1/[Os(VIII)] from the equation (7) gives

Slope = 
$$\frac{1}{K_1 K_2 K_3 [\text{ Glue}] [\text{ OH}^-]} + \frac{1}{K_2 K_3 [\text{ Glue}]}$$
.  
Intercept =  $\frac{1}{K_3 [\text{ Glue}]}$ 

According to Eqs. the values of  $K_1$ ,  $K_2$ , and  $K_3$  are calculated from the slope and intercept of such plot (Fig3) the reaction constants values obtained are  $K_1=19.12\times10^{-2}$  s<sup>-1</sup>,  $K_2=12.4\times10^5$  dm<sup>3</sup> mol<sup>-1</sup>, and  $K_3=8.12\times10^{-3}$  dm<sup>3</sup> mol<sup>-1</sup>.

It was reasonable consideration to compare the reactivity of Glue by CAT with catalyst under the same conditions monitored at different temperatures. A demonstrate the Arrhenius plot of log  $k_{\rm C}$  versus 1/*T* and the calculated activation parameters for the catalyzed reaction (Table 3). Moelwyn-Hughes [40] pointed out that in presence of the catalyst, the uncatalyzed and catalyzed reactions considred at the same time given the equation below

$$k_{\rm obs} = k_{\rm o} + k_{\rm C} [{\rm catalyst}]^x$$

Here  $k_{obs}$  is the observed pseudo first-order rate constant for the catalyst,  $k_0$  is the pseudo firstorder rate constant for the uncatalyzed reaction,  $k_C$  is represent the catalytic constant and x is the order of the reaction with respect to catalyst and x value was found to be unity. The values of  $k_C$ were calculated using the following equation.

$$k_{\rm obs} = k_{\rm o} + k_{\rm C}/[{\rm Ru}({\rm III})]$$

The proposed mechanisms is also supported by the observed values of the enthalpy of reaction  $\Delta H^{\#}$  and free energy of reaction  $\Delta G^{\#}$  were calculated obtain a high positive values of the free energy of activation and of the enthalpy of activation support the formation of highly solvated

transition state. The large negative value of  $\Delta S^{\#}$  indicates that complex (C) is more ordered than the reactants [41]. Further, the experimental observation shows had no effect and ionic strength on the rate of reaction, which also substantiates for the plausible mechanism.

### CONCLUSION

The simplified kinetic model is consistent and gives a reasonable response to experimental data. Among various species of CAT in alkaline medium, anion species TsNCI- from TsNHCl is considered as active species for the title reaction.In the present work we have studied the rates of oxidation of Glue by CAT catalyzed by Os(VIII) and their mechanistic pathway has been proposed. The results presented here clearly demonstrate that the oxidizing agent CAT was used for the oxidation of Glue catalyzed by Os(VIII) with complex formation which is more effective and inexpensive. The oxidation products are confirmed, 4-oxobutanoic acid and *p*toluenesulfonamide (TsNH2) by spot test and and FTIR and a possible reaction path for their formation is proposed. Activation parameters and the reaction constants were calcuated.The observed results have been explained from proposed mechanism and the rate law has been

### ACKNOWLEDGEMENT

This project was funded by (SABIC) and the Deanship of Scientific Research (DSR), King

Abdulaziz University, Jeddah, under grant no. (14/299/1433). The authors, therefore,

acknowledge with thanks SABIC and DSR technical and financial support.

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SCH. 1.



SCH. 2. A detailed mechanistic scheme for the Os(VIII) catalyzed oxidation of Glue with CAT in alkaline medium

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FIG. 1. (a)Chemical Strucure of Glue (b) The main product of 4-oxobutanoic acid



FIG. 2. (a)Optimized structure of Glue (b) Optimized structure of 4-oxobutanoic acid



FIG. 3.The log of the absorbance of oxidant plotted as a function of time for first order reactions at various CAT  $\times$  10-5 mol/dm3: (A) 1.0, (B) 3.0,(C) 5.0, (D) 8.0.



FIG. 4. Verification of rate law for the oxidation of Glue by CAT in the presence of catalyst.

### TABLE 1

Effect of varying CAT, Glue,OH-and Os(VIII)concentrations on the rate of reaction at 25°C

### (Scheme.1)

$K_{obs}$ (×10 <sup>4</sup> s <sup>-</sup>	$Os(VIII)(\times 10^5 mold)$	[OH-]	[Glue]	[CAT]
1)	$m^{-3}$ )	$(\times 10^3 \text{moldm}^{-3})$	$(\times 10^4 \text{moldm}^{-3})$	$(\times 10^3 \text{moldm}^{-3})$
6.21	1.0	1.0	0.5	1.0
6.20	1.0	1.0	1.0	2.0
6.21	1.0	1.0	2.0	5.0
6.21	1.0	1.0	3.0	7.0
6.20	1.0	1.0	4.0	10.0
4.18	0.5	1.0	0.5	5.0
5.12	0.6	1.0	1.0	5.0
6.21	0.1	1.0	2.0	5.0
6.18	2.0	1.0	3.0	5.0
6.16	3.0	1.0	4.0	5.0
3.18	1.0	0.5	2.0	5.0
4.89	1.0	0.6	2.0	5.0
5.31	1.0	0.8	2.0	5.0
6.21	1.0	1.0	2.0	5.0
8.34	1.0	2.0	2.0	5.0
2.38	0.5	1.0	0.5	5.0
4.22	0.6	1.0	1.0	5.0
6.21	0.1	1.0	2.0	5.0
12.15	2.0	1.0	3.0	5.0
18.42	3.0	1.0	4.0	5.0

### TABLE 2

Effect of varying dielectric constant (D) of the medium on the rate of reaction at 25°C

$k_{obs} \times 10^{-4}$	D	Percentage of MeOH (v/v)
8.45	76.5	0
7.65	70.0	10
5.88	65.2	20
4.56	60.7	30

 $[CAT] = 5.0 \times 10^{-3} \text{ mol } dm^{-3}; [Glue]o = 2 \times 10^{-4} \text{mol } dm-3; [OH] = 1.0 \times 10^{-3} \text{ mol } dm-3;$  $[Os(VIII)] = 1.0 \times 10^{-5} \text{ mol } dm-3.$ 

TABLE 3 Values of the catalytic constant  $(k_c)$  and activation parameters at different

temperatures

$k_C \times 10^4 (s^{-1})$	$1/T \times 10^{3}$	Temperature (K)			
4.52	3.413	293			
6.21	3.356	298			
7.35	3.300	303			
8.32	3.246	308			
Activation parameters					
	50.2				
	Ea (KJ mol)				
	$\Delta H^{-}$ (kJ mol <sup>-1</sup> )				
	$\Delta S^{\pm}(J K^{-1} mol^{-1})$				
	$\Delta G^{\pm}(kJ mol^{-1})$				